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GROWTH OF DIELECTRIC HfO_2/Ta_2O_5 THIN FILM NANOLAMINATE CAPACITORS BY ATOMIC LAYER EPITAXY

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Nanolaminates, i.e. layered structures with nanometer range constituent layer thickness, like Ta_2O_5/HfO_2 have been shown to possess high dielectric constant, low leakage current and high breakdown strength even after deposition at as low a temperature as 300 °C in Atomic Layer Epitaxy (ALE). The goal for this work was to make IC compatible RF capacitors without post-annealing. Large area (100 µm × 200 µm) 40 - 400 pF capacitors were fabricated with approximately 10 - 100 nm insulator thickness with good uniformity and yield. The nanolaminate structure could be etched in BCl_3/Cl_2 based reactive ion etching plasma with approximately 50 nm/min in single wafer processing. Thermal stability of the dielectric was studied at temperatures between 400 - 800 °C. Electrical properties of the capacitors were measured up to radio frequencies. The relative permittivity ε_r was in the order of 24 ±2 in all samples. The leakage current at 1 MV/cm was ≤ 1 µA/cm², and the breakdown strength 5 MV/cm at ≥ 30 nm film thickness

INTRODUCTION

The need for a new high dielectric material that would increase the capacitance storage capabilities in memory cells is widely known. One interesting candidate for such a high dielectric material is Ta_2O_5, which has a relative permittivity of 25. However, a thin film made from it tends to have high leakage current. Various post-deposition treatments, like annealing in oxygen atmosphere, have been studied to overcome this problem by introduction of silicon oxide underneath the tantalum oxide.

Another approach to the problem is to use thin layers of another material incorporated so that in fact one builds up a stack of thin films. This is so called nanolaminate (1-5). In case of tantalum oxide the role of the "other" material is to improve above all the leakage properties and the breakdown strength. When building a nanolaminate one has to be able to grow layers of different materials in one experiment and control the thicknesses of the individual films very accurately. Atomic Layer

Epitaxy, ALE, provides these features. A stack of different films, *i.e.* nanolaminate structure can easily be grown in one run and the thickness of the separate films is controlled simply by calculating the growth cycles.

The materials used for improving the dielectric properties of Ta_2O_5 have been HfO_2, ZrO_2, and Al_2O_3 (1-4). More complicated structures, like $(Nb_{1-x}Ta_x)_2O_5$-ZrO_2, have also been developed (4,5). A common feature to all of these ALE grown nanolaminates is that while they all still possessed a high dielectric constant, the leakage current as well as the charge storage factor could be vastly improved. These experiments were done on glass substrate with a structure thickness about 160 nm. The goal of the present study was to test thinner HfO_2/Ta_2O_5 nanolaminates and their feasibility in a real capacitor device.

The precondition for a successful growth of a nanolaminate is that all the materials can be crown using same growth conditions. The growth of both HfO_2 and Ta_2O_5 is done at 300 °C. One purpose of this study was also to find out the potential of the low temperature ALE process in realizing a metal-to-metal capacitor not requiring post-deposition thermal treatments.

The HfO_2/Ta_2O_5 nanolaminate films were test annealed in order to find out how well they sustain their amorphous nature. This was done in order to find out whether the back-end processing, Al-top electrode metallization and the growth of the passivation, layer at 425 °C would change the crystallinity of the nanolaminate structure. It is desirable that the structure retains its amorphous nature, since crystallization is known to flaw the electric properties of the nanolaminate (1).

A crucial part of making an IC device is etching. Accordingly a selective etching method had to be found for the HfO_2/Ta_2O_5 nanolaminate. Tantalum oxide can be etched with reactive ion etching (6-8). Literature concerning the etching of hafnium oxide is scarce and stating that the etching rate is very low (9,10). In fact HfO_2 is being reported as an etch stopper (10).

EXPERIMENTAL

The nanolaminate deposition was carried out in a modified F-120 ALE-reactor (Microchemistry Ltd., Espoo, Finland) The precursors were $TaCl_5$ and $HfCl_4$ for Ta_2O_5 and HfO_2, respectively. Water was used as an oxygen source. The reaction was carried out at a temperature of 300 °C and the reaction pressure was approximately 10 mbar.

For etching two types of equipment were tested, Lam AutoEtch 590 Oxide Etcher with fluorine plasma at 1000 W RF power and Plasma-Therm A360 Reactive Ion Etcher with chlorine plasma at RF power of 125 - 200 W.

The crystallinity and crystallic orientation of the Ta_2O_5/HfO_2 nanolaminate thin films were analysed with Philips 1880 powder x-ray diffractometer using CuK_α radiation

The capacitances were measured using HP 4192A LF Impedance Analyser and the current-voltage characteristics with HP 4145A Semiconductor Parameter Analyzer.

RESULTS AND DISCUSSION

The growth of the nanolaminate structure was carried out by ALE-method. By virtue of its operating principle the build up of a stack of different layers, *i.e.* a nanolaminate, by ALE is a straight forward task. After the growth rate of a material is determined the desired layer thickness can easily be achieved by multiplying the number of cycles with the growth rate. In this work 3 nm thick hafnium and tantalum oxide layers were used. The growth of the dual oxide nanolaminate was conducted simply by alternating the metal precursor pulses. Each sample consisted of a varying number of these sequentially deposited HfO_2 and Ta_2O_5 layers.

The thickness of each sample was determined by carefully measuring the growth rates per cycle for tantalum oxide and hafnium oxide with reflectometry and profilometry on specific calibration samples and by multiplying that with the number of cycles used. The exact thickness values and the sample structures can be seen in Table 1. Figure 1. a) depicts a schematic side view of the Ta_2O_5/HfO_2 nanolaminate structure. The overall thickness of the structure is in this case 15 nm. Figure 1 b) presents the structure of the capacitor fabricated in this work.

The 100 nm samples were annealed at 400, 500, 600, 700 and 800 °C for 60 min in nitrogen atmosphere to study the stability of the amorphous structure. After annealing at 700 °C the films showed some crystallinity. The LPCVD grown Ta_2O_5 thin films stayed also amorphous up to 700 °C (11). Hence half of all samples were annealed at 550 °C, ensuring that the amorphous nature is retained, to test the effect on dielectric properties. No significant differences were detected in electrical properties of annealed and non-annealed samples.

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Etching

The aim of the etching experiments was to find conditions where the etching rate of the HfO_2/Ta_2O_5 nanolaminate would be at practical level (> 50 nm/min) and that the required selectivities are achieved. The experiments were carried out by varying the gas concentrations in the plasma chamber. The etching was first tested with separate HfO_2- and Ta_2O_5-deposited wafers as well as with HfO_2/Ta_2O_5 nanolaminate prior to constructing the device.

Chlorine free fluorine plasma etching was tested in Lam AutoEtch 590 oxide etcher in the plasma mode using CF_4/CHF_3/He gas mixture. At 1000 W RF power resulting in silicon oxide etching at 700 nm/min, Ta_2O_5 was removed at a rate of 200 nm/min, but HfO_2 was not attacked. With added oxygen at flow rates between 0 - 20 sccm the erosion rate of HfO_2 remains below 2 nm/min. Hence it was concluded that HfO_2 cannot be removed using typical silicon oxide etching plasma.

Chlorine based etching was attempted in a reactive ion etcher Plasma-Therm A-360. Test wafers were etched using 200 W RF power, but later the power was finally tuned for patterned wafers. The influence of the different reactive gases, BCl_3, Cl_2, $CHCl_3$ and SF_6 as well as the influence of the pressure was studied by keeping the other parameters constant. The results are depicted in figs. 2 - 6. Both oxides behave in a very similar fashion in BCl_3, Cl_2 and $CHCl_3$ gas flows as well as for varying pressure. The etch rate of HfO_2 and Ta_2O_5 gets linearly higher with an increasing BCl_3 flow rate (fig. 2). The flow rates of Cl_2 and $CHCl_3$ have clear maximum values in etch rates. Both hafnium and tantalum oxides are being etched fastest when the flow rates for Cl_2 and $CHCl_3$ were 10 sccm. According to fig. 5 low processing pressure was advantageous for high etch rate, and does not show adverse effect on uniformity. The flow rate of SF_6 has a limited effect on the etch rate of Ta_2O_5 as show in fig. 6., but the etching of HfO_2 is practically stopped with SF_6 flow rate higher than 3 sccm. This is presumably due to formation of HfF_4, which is thermodynamically very stable compound.

Based on figs. 2 - 6 the final etching parameters were determined as follows: BCl_3: 60 sccm, Cl_2: 10 sccm, $CHCl_3$: 10 sccm and p: 100 mtorr. The etch rate was about 50 nm/min at applied 125 W power. The power setting was limited by the photoresist.

Dielectric properties

The measured dielectric properties of the nanolaminates are presented in Table 1. The values are mean values of two samples, one as-grown and the other one post annealed at 550 °C for 1 hour in nitrogen atmosphere. The post treatment did not show any effect on the measured values. Also the layer sequence, *i.e.* HfO_2 or Ta_2O_5, as the bottom or top layer did not affect the dielectric properties. Figure 7. shows capacitance and inverted capacitance vs. insulator thickness. The inverted capacitance has a linear dependence on the thickness, hence the nanolaminates were vertically of uniform quality.

The relative permittivity was in all samples 22 - 26 and shows no dependence from the nanolaminate thickness. The ε_r-value was also constant with frequency at least up to f = 1GHz with no specific loss mechanism. The leakage current was below 1 nA in samples thicker than 29 nm. Figure 8 depicts log I as a function of voltage for a 35 nm thick sample. The thin ones, 16 and 13 nm had an increasing value, the 13 nm clearly being rather leaky. The breakdown strength decreased with decreasing thickness. The increased leakage current and decreased breakdown strength in thinner films was possible due to small microscopic particles produced during the hafnium oxide deposition. The formation of these particles was discovered found out in the course of this work. The origin being eventually in the hafnium precursor or in the deposition conditions.

Table 1. The number of the deposited layers in the HfO_2/Ta_2O_5-nanolaminate structure, overall thickness of the structure, capacitance, relative permittivity, leakage current and breakdown strength. The capacitor area was 100 × 200 μm^2.

# layers	Thickness (nm)	C (pF)	ε_r	I@1MV/cm	E_{br} (MV/cm)
34	108	42	26	≤ 1 nA	5
33	105	40	24	≤ 1 nA	5
10	32	131	24	≤ 1 nA	4.9
9	29	143	24	≤ 1 nA	3.9
5	16	241	22	3 nA	3.5
4	13	372	26	3 μA	2.4

CONCLUSION

Ta_2O_5/HfO_2 nanolaminate capacitors with different thicknesses were grown by Atomic Layer Epitaxy-method. The structure could be dry etched with selectivity requirements fulfilled. The nanolaminate was thermally adequately stable to tolerate the back-end processing cycles. The dielectric properties of the Ta_2O_5/HfO_2 capacitors were good. The permittivity was high (24) and independent of the total nanolaminate thickness. The leakage current was low except in very thin thin nanolaminates.

ACKNOWLEDGEMENTS

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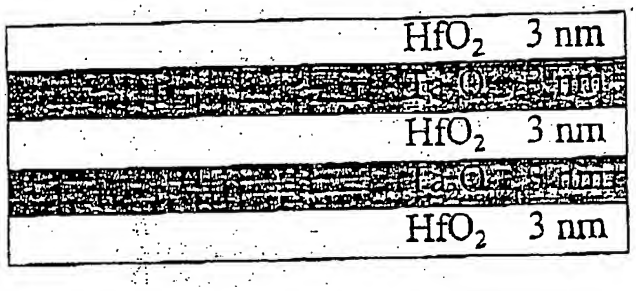

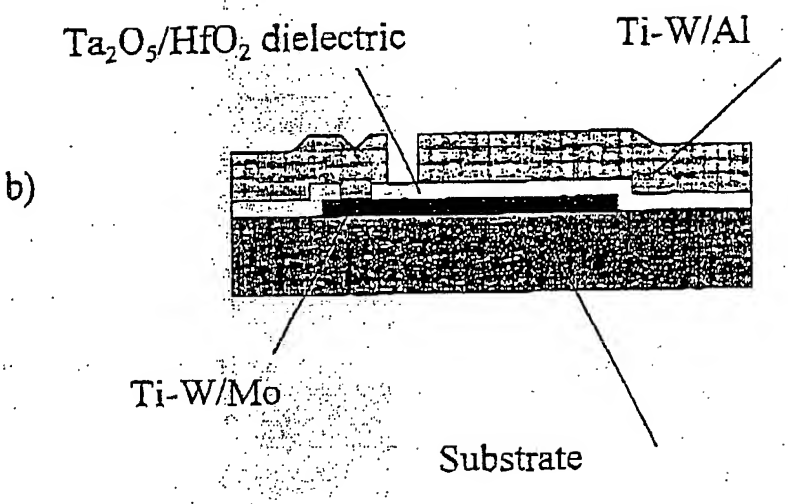

Figure 1. a) Schematic side-view of a Ta_2O_5/HfO_2 thin film five-layer nanolaminate structure with a layer thickness of 3 nm each and with 15 nm overall thickness of the structure. b) The structure of the Ta_2O_5/HfO_2 capacitor. The area was 100 × 200 μm^2. The bottom electrode was Mo with a Ti-W interlayer between the Si-substrate and the electrode. The top electrode was Al with Ti-W interlayer between the dielectric and the electrode.

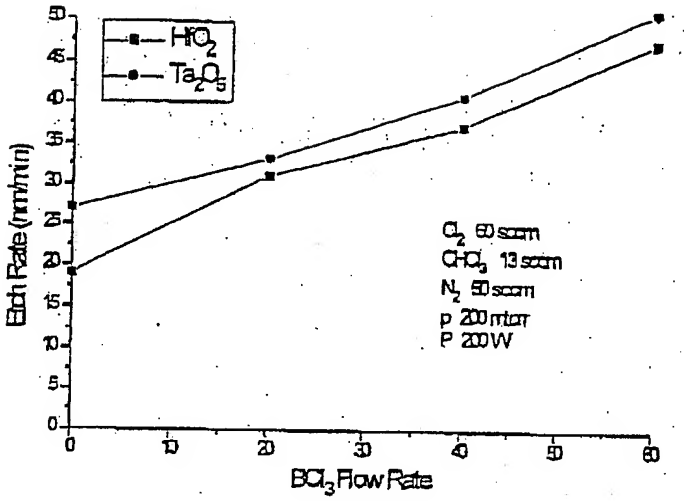

Figure 2. The etching rate of HfO_2 and Ta_2O_5 as a function of BCl_3 flow rate.

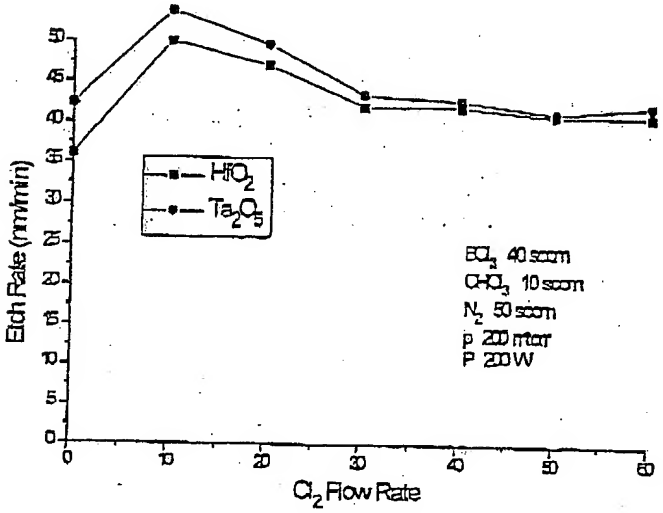

Figure 3. The etching rate of HfO_2 and Ta_2O_5 as a function of Cl_2 flow rate.

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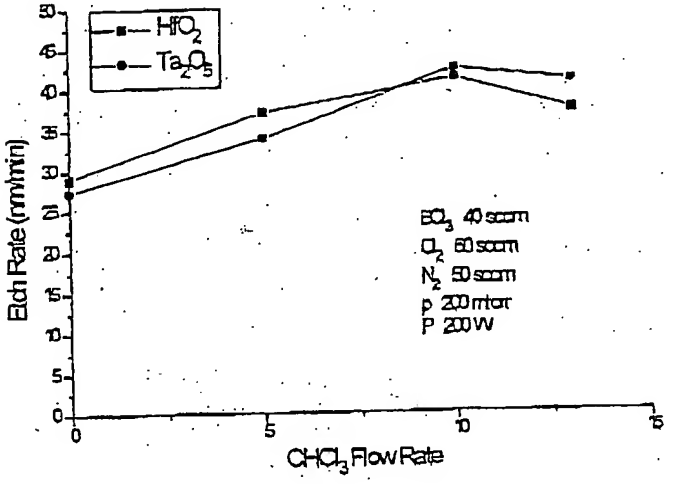

Figure 4. The etching rate of HfO_2 and Ta_2O_5 as a function of $CHCl_3$ flow rate.

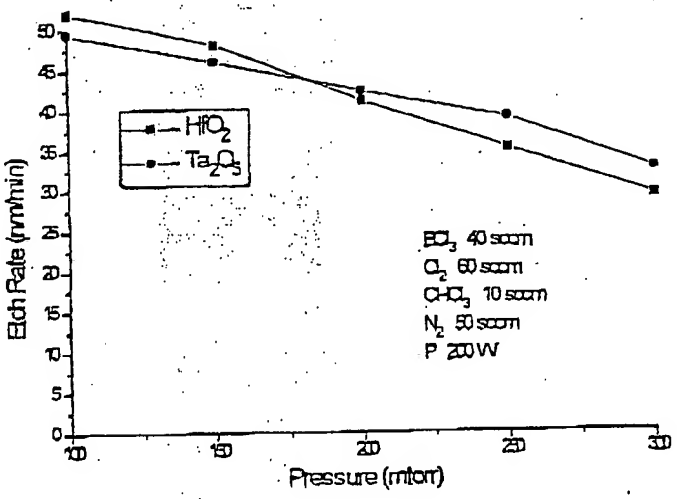

Figure 5. The etching rate of HfO_2 and Ta_2O_5 as a function of pressure.

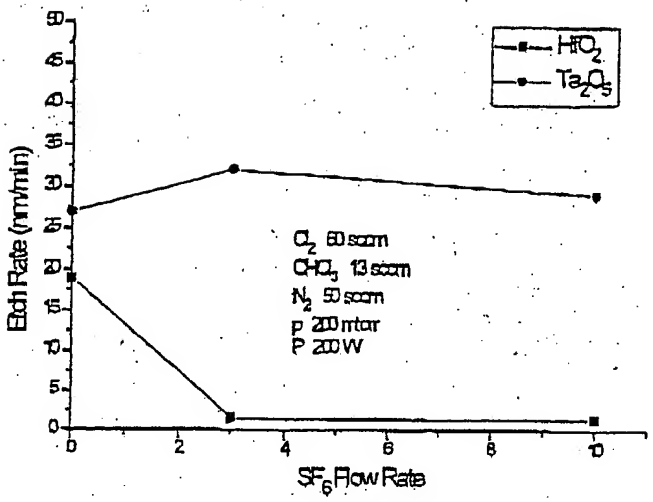

Figure 6. The etching rate of HfO_2 and Ta_2O_5 as a function of SF_6 flow rate.

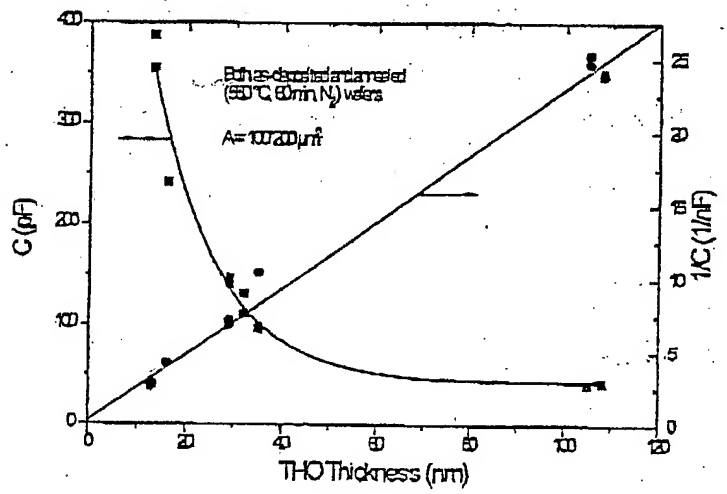

Figure 7. Capacitance and inverted capacitance vs. insulator thickness

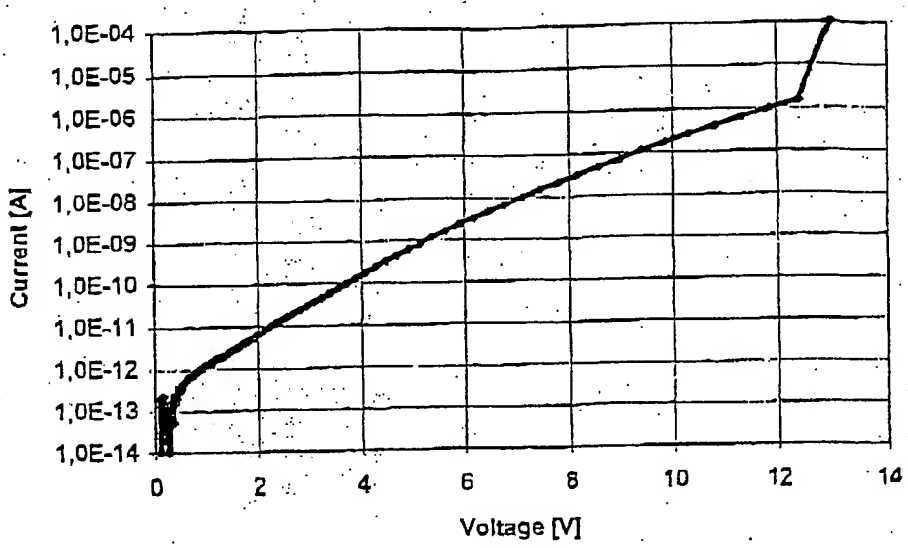

Figure 8. Electrical leakage for 35 nm thick Ta_2O_5/HfO_2 capacitor of 100 × 200 μm^2